Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 738

Lignin Structural Changes by Oxidative Alkaline Extraction

T.M. Runge, A.J. Ragauskas, and T.J. McDonough

July 1998

Submitted to
1998 TAPPI Pulping Conference
Montreal, Quebec, Canada
October 25–29, 1998

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is a unique organization whose charitable, educational, and scientific purpose evolves from the singular relationship between the Institute and the pulp and paper industry which has existed since 1929. The purpose of the Institute is fulfilled through three missions, which are:

- to provide high quality students with a multidisciplinary graduate educational experience which is of the highest standard of excellence recognized by the national academic community and which enables them to perform to their maximum potential in a society with a technological base; and
- to sustain an international position of leadership in dynamic scientific research which is participated in by both students and faculty and which is focused on areas of significance to the pulp and paper industry; and
- to contribute to the economic and technical well-being of the nation through innovative educational, informational, and technical services.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

Lignin Structural Changes by Oxidative Alkaline Extraction.

T. M. Runge, Graduate Student
A. J. Ragauskas, Professor
T. J. McDonough, Professor

Institute of Paper Science and Technology
500 10th Street NW
Atlanta, GA 30318

ABSTRACT

The research presented compares the effects of oxygen and hydrogen peroxide reinforcement in an alkaline extraction stage on lignin degradation using a chromatographic technique, which measures apparent molecular weight. These data, together with extent of delignification, cellulose degradation, and bleached brightness data, were used to provide insight into the types of lignin degradation reactions occurring. The combined data suggests oxygen and hydrogen peroxide react with both residual and dissolved lignins. Since oxidant reactions with dissolved lignins represent a waste of bleaching chemicals, alternative extraction stages were investigated. The purpose of the alternative stages was to preferentially direct the oxidants to react with the residual lignin. These alternative stages represent the first step in research directed towards a more efficient alkaline extraction stage.

INTRODUCTION

The recent promulgation of the Cluster Rules has increased pulp mills' use of elemental chlorine free (ECF) bleach sequences, such as D(EOP)DED. One stage that has received little research attention is the oxidative alkaline extraction stage, (EOP). An oxidative alkaline extraction stage is defined as a sodium hydroxide stage with hydrogen peroxide and/or oxygen added. Oxidative alkaline extraction stages are worth studying since they are responsible for the bulk of the lignin removal that occurs in the bleaching sequence. Also, with the added oxidants, extraction stages have complicated chemistry that may offer opportunities for beneficial modification.

This paper reports findings on the structural changes in lignin caused by oxidative alkaline extraction stages. The findings suggest that a portion of the oxidant is consumed by reactions with dissolved lignin. Since these reactions represent a loss of chemical, several alternative stages were studied, with the goal of forcing oxidants to react only with the residual lignin. One of the modified stages investigated was a counter-current extraction stage designed to have the highest concentration of oxidant interact with pulp containing only residual lignin. This concept is borrowed from modified continuous cooking (MCC) of kraft pulp. MCC utilizes counter-current zones, removal of dissolved lignins, and a high concentration of pulping chemicals at the end of the cook to favor reactions with residual lignin [1].

The other modified stage investigated was a double extraction, which is similar to the Papricycle extraction process. A Papricyle extraction uses the sodium carbonate and bicarbonate formed from the alkaline extraction to pre-extract the pulp before the alkaline extraction stage. Although this process requires an additional washer, it provides the benefit of caustic savings. Studies indicate that converting conventional and oxygen reinforced alkaline extraction stages to the Papricycle process provide a 30% caustic reduction with no change in delignification or latter stage brightness [2, 3, 4, 5].

Exploring alkaline extraction chemistry starts with the examination of the alkali's role in the extraction. The alkali stage removes lignin primarily by ionizing carboxylic acid and phenolic groups, making them more alkali-soluble. The alkaline environment also decreases lignin's hydrodynamic volume, allowing greater diffusion from the cell wall [6, 7]. Several sodium hydroxide reactions with lignin increase the solubility of the lignin. These reactions include: (1) nucleophilic displacement of organically bound chlorine, which also reduces AOX [8, 9], (2) saponification of muconic acid methyl ester structures formed in the previous D stage [10], and (3) nucleophilic addition of hydroxide ions to quinone structures [9, 11]. The nucleophilic addition, which results in either a

hydroxy-substituted catechol or a carboxylic acid substituted cyclopentadiene, has only been observed in model compounds, possibly due to the low content of quinone structures in lignin contained in pulp.

The addition of oxygen and hydrogen peroxide reinforcement to alkaline extraction stages provides additional delignification and brightness gains. Oxygen is believed to react with lignin primarily through auto-oxidation of phenolic groups [12, 13, 14]. Hydrogen peroxide in the form of the hydroperoxide anion reacts primarily with lignin carbonyl structures. The mechanism involves the formation of organic hydroperoxide anions, which rearrange with the cleavage of carbon-carbon bonds [9, 15]. The cleavage may open aromatic rings, allowing them to be further degraded through Michael addition reactions to low molecular weight carboxylic acid structures.

Although several fundamental studies exist looking at oxygen and hydrogen peroxide reactions with lignins, their specific application as reinforcement in an alkaline extraction stage for chlorine dioxide delignified pulp has not been extensively studied. This paper contributes to this area, by studying structural changes to lignin during various oxidative alkaline extraction conditions.

EXPERIMENTAL PROCEDURES

Bleaching Conditions

Kraft pulps were bleached with chlorine dioxide (D_0 stage) followed by an alkaline extraction. The chlorine dioxide stage was performed in a Quantum Technologies mixer. A kappa factor (defined as total active chlorine charge/kappa number) of 0.20 was used. The pulps, at 10% consistency, were preheated to 45°C in the mixer. Dilute sulfuric acid was used to adjust the pH of the pulps so that the final pH would be approximately 2.0. Aqueous chlorine dioxide was added to the pulps while the pulp was stirred. The pulps were allowed to react for 45 minutes with interval mixing every 2 minutes. The pulps were removed from the reactor and thoroughly washed with filtered deionized (DI) water. The alkaline extraction was performed immediately after washing the ClO_2 bleached pulp. The extraction was done in a continuously stirred reactor at 70°C for 75 minutes using the chemical charges shown in Table 1.

Table 1. Alkaline Extraction Conditions

Bleaching Stage	Bleaching Conditions Employed[a]
E	2.0% NaOH, performed under atmospheric pressure.
(EO)	2.5% NaOH, 60 psig initially, decreasing 12 psig/5 minutes, final 50 minutes were performed at atmospheric pressure.
(EP)	2.5% NaOH and 0.5% hydrogen peroxide.
(EPO)	2.5% charge of NaOH, 0.5% hydrogen peroxide, 60 psig initially, decreasing 12 psig/5 minutes, final 50 minutes performed at atmospheric pressure.
(EAr)	All oxygen was removed from the pulp and chemicals via a freeze-thaw cycle. 2.0% NaOH was used, and the reactor was slightly pressured with argon (10 psig) to prevent the introduction of O_2 into the reactor.

[a]The charge of NaOH employed was selected to ensure that the terminal pH was > 10.5

Counter-current (EP) Stage

The counter-current alkaline extraction stage was performed at lab scale using columns of pulp to simulate a counter-current reactor. The reactor, shown with a simple schematic in Figure 1, consisted of several plastic (PVDF) 400mL cylinders packed with 50g of pulp at 25% solids. Five cylinders were connected in a series with Nalgene tubing and quick-connect fittings. Water was pumped through the bottom of the last column using a peristaltic pump. NaOH and H_2O_2 were added through a second peristaltic pump into the next-to-last column. After 15 minutes, an additional column was introduced into the beginning of the series, the columns were moved sequentially down and the last column was removed. The movement of columns in the opposite direction to the

liquid phase simulates a counter-current reactor tower. Adjusting NaOH and H_2O_2 ratios and flow, a 2.5% NaOH charge and 0.5% H_2O_2 charge were applied to the pulp. During the reaction, the consistency of the pulp was calculated to be approximately 3%. Consistencies higher than 3% were not possible due to excessive backpressure in the system, caused by friction from pulp packed into the columns. The entire reactor was immersed in a water bath to keep the reaction at 70°C.

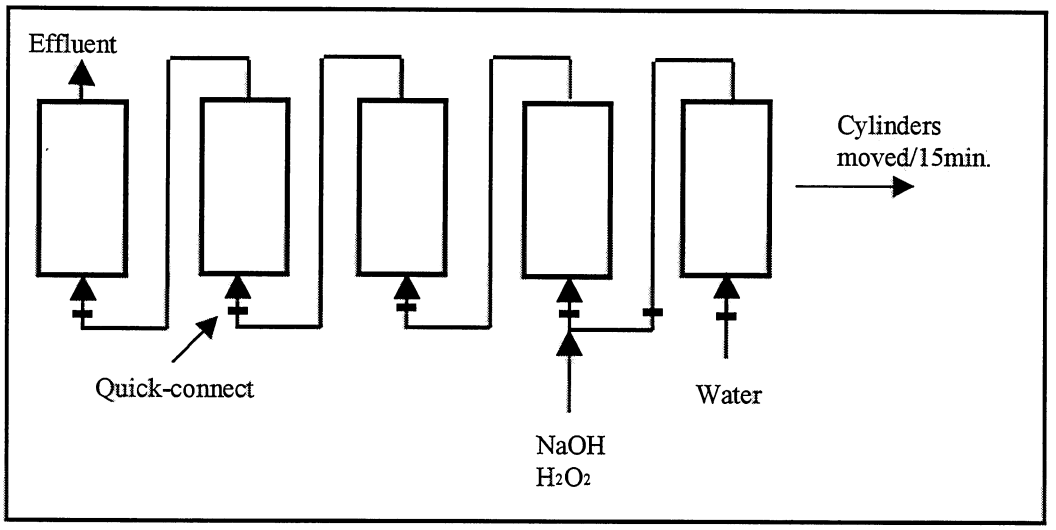

Figure 1. Simulated Counter-current Reactor Schematic

Pulp and Effluent Characterization

Pulps were characterized using a 1/4 kappa test method [16, 17]. Carbohydrate degradation was measured indirectly by solvating the pulp in cupriethylenediamine (CED) and measuring the solution's viscosities with a capillary viscometer [18]. Standard TAPPI brightness handsheets were made at 240 g/m^2 from the D_1 pulp [19], and used to measure ISO brightness of the pulps.

Effluent molecular weights were measured by an aqueous gel permeation chromatography (GPC) method [20]. The method involves passing effluent through two Sephadex columns using an aqueous 0.1 M LiCl eluent and a total organic carbon (TOC) detector. Effluents were analyzed without dilution. Effluents containing a low amount of organic matter were concentrated before analysis. The column was calibrated using polyethylene glycol standards and methanol (giving a calibration range for molecular weights of 32 to 19,700). Number average molecular weight (MW_N) and weight average molecular weight (MW_W) were calculated using Equations 1 and 2. A statistical analysis was performed on the apparent molecular weight averages by analyzing 4 separate DE bleach effluents. The least significant difference values at a 95% confidence interval for MW_N and MW_W were calculated to be 621 and 718 respectively.

$$MW_W = \sum w_i M_i \quad (1)$$

$$MW_N = \sum x_i M_i \quad (2)$$

where: w_i is the weight fraction of fraction i
x_i is the mole fraction of fraction i
M_i is the molar mass of fraction i

RESULTS AND DISCUSSION

Conventional Oxidative Alkaline Extraction

A comparison of the pulp properties from oxidant reinforcement is shown in Table 2. The oxygen and hydrogen peroxide reinforcements increase delignification and D_1 ISO brightness as expected. Hydrogen peroxide gave an increase in brightness that was significantly more than that achieved with oxygen reinforcement.

Table 2. Conventional Alkaline Extraction Pulp Properties

Bleaching Sequence	Kappa # *(CI)*[a]	CED Viscosity *(CI)*	D_1 ISO brightness *(CI)*
Brownstock	30.4 *(± 0.29)*	30.3 *(± 0.50)*	N/A
D	14.7 *(± 0.17)*	26.7 *(± 0.29)*	N/A
D(EAr)	7.10 *(± 0.29)*	25.7 *(± 0.50)*	73.6 *(± 0.61)*
DE	6.50 *(± 0.17)*	22.8 *(± 0.29)*	75.6 *(± 0.35)*
D(EO)	4.20 *(± 0.29)*	20.1 *(± 0.50)*	76.5 *(± 0.61)*
D(EP)	4.97 *(± 0.17)*	22.3 *(± 0.29)*	80.5 *(± 0.35)*
D(EPO)	3.30 *(± 0.29)*	20.4 *(± 0.50)*	84.1 *(± 0.61)*

[a] CI describes a 95% confidence interval from a pooled variance. This value was obtained with 3 replicates for the D, DE, and D(EP) pulps (3 tests/sample for kappa, 2 tests/sample for CED viscosity, 4 tests/sample for ISO Brightness)

Molecular weight distributions were measured for the alkaline extraction stage effluents, and the weight and number averages were calculated. The results are shown in Table 3. The values depict a decrease in the effluent molecular weight with increased oxidant reinforcement. Molecular weight decreases were believed to be due to lignin chain cleavage from oxidation reactions with oxygen and hydrogen peroxide. However, it was questioned whether the applied oxidant was reacting with lignin remaining in the fiber or with dissolved lignin. This question becomes important as oxidation of the dissolved lignins represents a waste of oxidant reinforcement, since this lignin is already free of the fiber. Considering that the dissolved lignin content is higher than the residual lignin content, the potential amount of oxygen and hydrogen peroxide that could be wasted becomes significant.

Table 3. Effluent Apparent Molecular Weight Averages

Bleaching Sequence	MW_N	MW_W	Polydispersity
D(EAr)	3839	8061	2.10
DE	3292	7121	2.17
D(EO)	2579	6618	2.57
D(EP)	2662	5984	2.25
D(EPO)	1987	4889	2.46

An experiment was performed to determine whether oxygen and hydrogen peroxide were reacting with dissolved or residual lignin. The experiment consisted of treating effluent from an oxidant free alkaline extraction stage with oxygen and/or hydrogen peroxide with the same charges as done when pulp was present. The molecular weight distribution of the oxidant-treated effluent was then measured. The resulting data, shown in Table 4, indicates the oxidant treatment decreased the molecular weight averages of the effluent to approximately the same level as when pulp was present. This implies the molecular weight decrease observed with oxidant reinforcement is due to oxygen and hydrogen peroxide reacting with effluent lignin. A further implication is that a portion of the oxidant reinforcement is wasted reacting with dissolved lignin.

Table 4. Oxidized Effluent Apparent Molecular Weight Averages

Bleaching Sequence	MW_N	MW_W	Polydispersity
D(EAr)	3839	8061	2.10
D(EAr) (EO)	2804	5768	2.06
D(EAr) (EP)	3130	6592	2.11
D(EAr) (EPO)	2072	4442	2.14

The research project attempted to discover how much oxidant is consumed reacting with dissolved lignin by performing alternative extraction sequences. These sequences were designed to remove the majority of the dissolved lignin before applying oxygen or hydrogen peroxide. Removing the lignin dissolved by alkali alone should increase the amount of oxidant able to react with the residual lignin, and thus should increase delignification and brightness.

Counter-current Alkaline Extraction

The first alternative stage designed to avoid consumption of oxidant reinforcement by dissolved lignin was a counter-current alkaline extraction stage. The reason for using this type of reactor is that the oxidant is applied to the pulp at a point that the pulp suspension contains primarily residual lignin. A lab-scale reactor was built to simulate a counter-current reactor. The design of the counter-current reactor did not provide for mixing or consistency to batch reactors comparable to that used in simulating conventional alkaline extraction stages. Because of these factors, an alkaline extraction stage was performed with the pulp and chemical running co-currently to serve as a control. The co- and counter-current alkaline extraction stages were carried out with hydrogen peroxide reinforcement only as the reactor could not withstand pressures of oxygen reinforcement.

The pulps produced in the counter-current extraction were characterized with respect to delignification and carbohydrate degradation. Portions of the pulps were further reacted in a D_1 stage and characterized for brightness. The results show only a small difference between the counter-current and co-current control. This suggests the amount of oxidant being wasted on the dissolved lignin was small. It is also possible that the residual lignin was unreactive to the additional oxidant reinforcement made available by limiting its reaction with dissolved lignin.

Table 5. Counter-current Alkaline Extraction Pulp Properties

Bleaching Sequence	Kappa *(CI)*[a]	Viscosity *(CI)*	D_1 ISO brightness *(CI)*
D(E+P) Co-current	7.1 *(± 0.30)*	21.0 *(± 0.98)*	75.6 *(± 1.32)*
D(E+P) Counter-current	6.4 *(± 0.18)*	21.8 *(± 0.57)*	75.7 *(± 0.76)*

[a] CI describes a 95% confidence interval from a pooled variance. This value was obtained with 3 replicates for the D(E+P) Counter-current stages (3 tests/sample for kappa, 2 tests/sample for CED viscosity, 4 tests/sample for ISO Brightness)

Effluent molecular weight averages from the counter-current and co-current stages were measured (Table 6). The data show higher molecular weight averages for the counter-current, which suggest less hydrogen peroxide was consumed by the dissolved lignin. The data also showed both the co- and counter-current stages to have higher apparent molecular weight than the batch D(EP). It is postulated the differences between the reactors previously discussed could cause the batch reactor to have lower molecular weight averages, as the hydrogen peroxide may have been more reactive in the batch reactor.

Table 6. Counter-current Stage's Effluent Apparent Molecular Weight Averages

Bleaching Sequence	MW_N	MW_W	Polydispersity
D(E+P) Co-current	3854	7245	1.88
D(E+P) Counter-current	3956	7809	1.97
D(E+P) batch	2662	5984	2.25

Summarizing the counter-current reaction data, one can conclude that removing the dissolved lignin before applying the hydrogen peroxide did not increase delignification or brightness. This indicates either little hydrogen peroxide is lost reacting with dissolved lignin or the residual lignin is unreactive to extra hydrogen peroxide.

Double Alkaline Extraction

A second set of experiments consisted of performing two alkaline extraction stages in a series. The double extraction stage consisted of a first extraction done with only NaOH to remove the majority of the lignin. The pulp was washed and then submitted to a second alkaline extraction with oxygen and peroxide reinforcement. The double extraction stage should provide a measure of the amount of oxidant that is wasted on the dissolved lignin in the effluent.

The control for the double extraction stage was another double extraction stage, which was performed in reverse order (an (EPO) stage followed by an E stage). The reversed double extraction stage was chosen as the control instead of a batch (EPO) stage to remove leaching effects from extra alkali addition. The results (Table 7) were similar to those of the counter-current reactions, with no significant gains in delignification or brightness. This again implies either a significant portion of oxygen and hydrogen peroxide is not consumed by the dissolved lignin, or the residual lignin is unreactive to increased oxidant.

Table 7. Double Alkaline Extraction Pulp Properties

Bleaching Sequence	Kappa *(CI)*[a]	Viscosity *(CI)*	D_1 ISO brightness *(CI)*
D(EPO)E	4.0 *(± 0.30)*	20.5 *(± 2.41)*	84.6 *(± 1.51)*
D(E)(EPO)	3.7 *(± 0.18)*	21.5 *(± 1.39)*	85.6 *(± 0.87)*

[a] CI describes a 95% confidence interval from a pooled variance. This value was obtained with 3 replicates for the D(EPO)E bleach condition (3 tests/sample for kappa, 2 tests/sample for CED viscosity, 4 tests/sample for ISO Brightness)

Apparent molecular weight averages were measured for both the initial and secondary stages of the double extraction stages. The results, shown in Table 8, indicate that when the oxidant was present in the first alkaline extraction stage the effluent molecular weight was decreased. The data also shows the second alkaline extraction stage to be removing larger fragments than the first alkaline extraction stage possibly due to a leaching effect. Larger lignin fragments may take additional time to diffuse out of the fiber cell wall. These fragments would become enriched in the fiber cell during the first alkaline extraction, which would increase the molecular weight average of the second alkaline extraction stage.

Table 8. Double Extraction Sequence's Filtrate Apparent Molecular Weight Averages

Bleaching Sequence	MW_N	MW_W	Polydispersity
E stage of DE	3303	7068	2.14
(EPO) stage of DE(EPO)	3214	8898	2.77
(EPO) stage of D(EPO)	2051	4859	2.37
E stage of D(EPO)E	3112	7912	2.54

The increased molecular weight average for the second alkaline extraction stage was noted even for the second stage containing oxidant reinforcement. It was believed the oxidants improved delignification by cleaving the residual lignin into small enough fragments so that they are alkali soluble. This cleavage should result in lower molecular weight averages for the (EPO) portion of an E(EPO) double extraction stage. This did not happen. It is possible the residual lignin after the E portion of an E(EPO) stage is highly condensed and not susceptible to cleavage. Oxidation from oxidant reinforcement could increase the solubility of the residual lignin without decreasing the lignin's chain length.

Varying Hydrogen Peroxide Charge

The counter-current and double extraction stages both indicated that removing the dissolved lignin does not significantly increase delignification or brightness. This implies that either only a small portion of oxidant is consumed by the dissolved lignin, or the residual lignin is unreactive to increased oxidant. To determine which scenario was the case, a series of alkaline extraction stages with varying charges of hydrogen peroxide were performed. The results shown in Table 9 indicate increased oxidant is capable of further delignification and increased brightness. This suggests the amount of oxidant reinforcement wasted on the dissolved lignin in the effluent is less than the oxidant equivalent of a 0.15% hydrogen peroxide charge.

Table 9. Varying Hydrogen Peroxide Charge in (EP) Extraction Pulp Properties

H_2O_2 applied in (EP) stage	H_2O_2 consumed in (EP) stage	Kappa *(CI)*[a]	Viscosity *(CI)*	D_1 ISO brightness *(CI)*
0.20%	0.20%	6.4 *(± 0.47)*	23.4 *(± 0.92)*	74.18 *(± 1.27)*
0.35%	0.35%	5.3 *(± 0.47)*	22.4 *(± 0.92)*	79.41 *(± 1.27)*
0.50%	0.50%	5.0 *(± 0.27)*	22.3 *(± 0.53)*	80.50 *(± 0.73)*
0.65%	0.64%	4.1 *(± 0.47)*	21.6 *(± 0.92)*	81.74 *(± 1.27)*
0.80%	0.75%	3.6 *(± 0.47)*	22.2 *(± 0.92)*	82.36 *(± 1.27)*

[a] CI describes a 95% confidence interval from a pooled variance. This value was obtained with 3 replicates for the D(EP) at 0.50% bleach condition (3 tests/sample for kappa, 2 tests/sample for CED viscosity, and 4 tests/sample for ISO Brightness)

CONCLUSIONS

Oxidant reinforcement in the alkaline extraction provides means for improving delignification and brightness. GPC experiments demonstrated a loss in molecular weight of the effluent lignin, which was theorized to be due to oxygen and hydrogen peroxide reacting with dissolved lignin. Two alternative alkaline extraction stages, a counter-current stage and a double extraction stage, were performed to force the oxidants to react only with the residual lignin. Both experiments showed no significant gains over the standard oxidative alkaline extraction suggesting the amount of oxidant being consumed by dissolved lignin was small or that the residual lignin left after the alkaline extraction stage was unreactive to additional oxidant. Additional experiments were performed with alkaline extraction stages done with varying charges of hydrogen peroxide. These experiments indicated the residual lignin to be reactive with additional hydrogen peroxide. This indicates the amount of oxidant lost was less than a charge of 0.14% H_2O_2.

This paper started with the observation that a decrease in effluent molecular weight occurs with oxidant reinforcement. It was hypothesized that a portion of the oxidant was reacting with dissolved lignin. Further experimentation has shown the amount lost to be a small quantity. These facts lead to the hypothesis that a small portion of oxidant reinforcement is capable of cleaving the lignin polymer chain. The amount of oxidant lost in these reactions is small enough that alternative oxidative extraction stages are not necessary.

ACKNOWLEDGMENTS

The authors thank the Institute of Paper Science and Technology and its member companies for financial support. The authors also wish to thank Dr. Don Dimmel for valuable discussions of the research. T. M. Runge will use portions of this work as partial fulfillment of Ph.D. degree requirements at the Institute of Paper Science and Technology.

REFERENCES

1 Johansson, B.; Mjoberg, J.; Sandstrom, P.; Teder, A. Modified Continuous Kraft Pulping – Now a Reality. Svensk Paperstidning, 87(10) 30-35 (1984).

2 Berry, R.M.; Fleming, B.I. Using Extraction-Stage Filtrate to Preextract Chlorinated Pulp. Journal of Pulp and Paper Science, 14(5): J121-J124 (1988).

3 Berry, R.M.; Fleming, B.I. The Chemistry of Papricycle. Journal of Pulp and Paper Science, 15(5): J165-J169 (1989).

4 Berry, R.M.; Fleming, B.I.; Berndt, G.; Williams, G. Papricylce – a Mill-proven Process for Saving Bleach Plant Caustic and Steam. Tappi Journal, 72:109-113 (1989).

5 Berry, R.M.; Fleming, B.I. Papricycle: Its Effectivenes in Bleaching with an Eo stage. Appita Journal, 43(6): 426-428 (1990).

6 Rudatin, S; Sen, Y.L.; Woerner, D.L. Association of Kraft Lignin in Aqueous Solutions. Lignin Properties and Materials. ACS Symposium Series 397. Edited by W. Glasser and S. Sarkanen, 1989, p.145-154.

7 Dutta, S.; Garver, T.; Sarkanen, S. Modes of Association between Kraft Lignin Components. Association of Kraft Lignin in Aqueous Solutions. Lignin Properties and Materials. ACS Symposium Series 397. Edited by W. Glasser and S. Sarkanen, 1989, p.155-176.

8 Braddon, S.A.; Dence, C.W. Structure and Reactivity of Chlorolignin. Tappi Journal, 51(6):249-256 (1968).

9 Dence, C.W. Chemistry of Chemical Pulp Bleaching. Pulp Bleaching - Principles and Practices. Edited by D.W. Reeve and C.W. Dence. TAPPI PRESS, Atlanta, 1996, p.125-153.

10 Runge, T.; Ragauskas, A.; Froass, P. Advances in Understanding the Basics of the First Alkaline Extraction Stage in Bleaching. 1997 Pulping Conference, San Francisco. TAPPI PRESS, Atlanta, 1997, p.603-608.

11 Gierer, J. Chemistry of Delignification Part 2: Reactions of Lignins During Bleaching. Wood Science and Technology 20, 1-33 (1986).

12 Gierer, J. Mechanisms of Bleaching with Oxygen-Containing Species. 1987 International Symposium on Wood and Pulping Chemistry Proceedings, Vol. 1, Paris, CPPA, Montreal, 1987, p.279-288.

13 Eckert, R.C.; Chang, H.M.; Tucker, W.P. Oxidative Degradation of Phenolic Lignin Model Compounds with Oxygen and Alkali. Tappi Journal, 56(6):134-138 (1973).

14 , Kratzl, K.; Claus, P.; Lonsky, W.; Gratzl, J.S. Model Studies on Reactions Occuring Oxidations of Lignin with Molecular Oxygen in Alkaline Media. Wood Science Technology, 8(1):35-49 (1974).

15 Gierer, J.; Imsgard, F. Reactions of Lignins with Oxygen and Hydrogen Peroxide in Alkaline Media. Svensk Papperstidning, 80(16): 510-518 (1977).

16. TAPPI Test Methods 1996-1997. T 236 om-85. TAPPI PRESS, Atlanta, 1996.

17. TAPPI Test Methods 1996-1997. T 222 om-88. TAPPI PRESS, Atlanta, 1996.

18. TAPPI Test Methods 1996-1997. T 230 om-94. TAPPI PRESS, Atlanta, 1996.

19. TAPPI Test Methods 1996-1997. T 272 om-92. TAPPI PRESS, Atlanta, 1996.

20. Schwantes, T.A.; McDonough, T.J. Development of a Method of Aqueous Gel Permeation Chromatography for the Determination of Molecular Weight Distributions of Bleaching Effluents. 1994 International Environmental Conference. TAPPI PRESS, Atlanta, 1994. p.683-695.